Reductant Formation for NOx Reduction

AIChE

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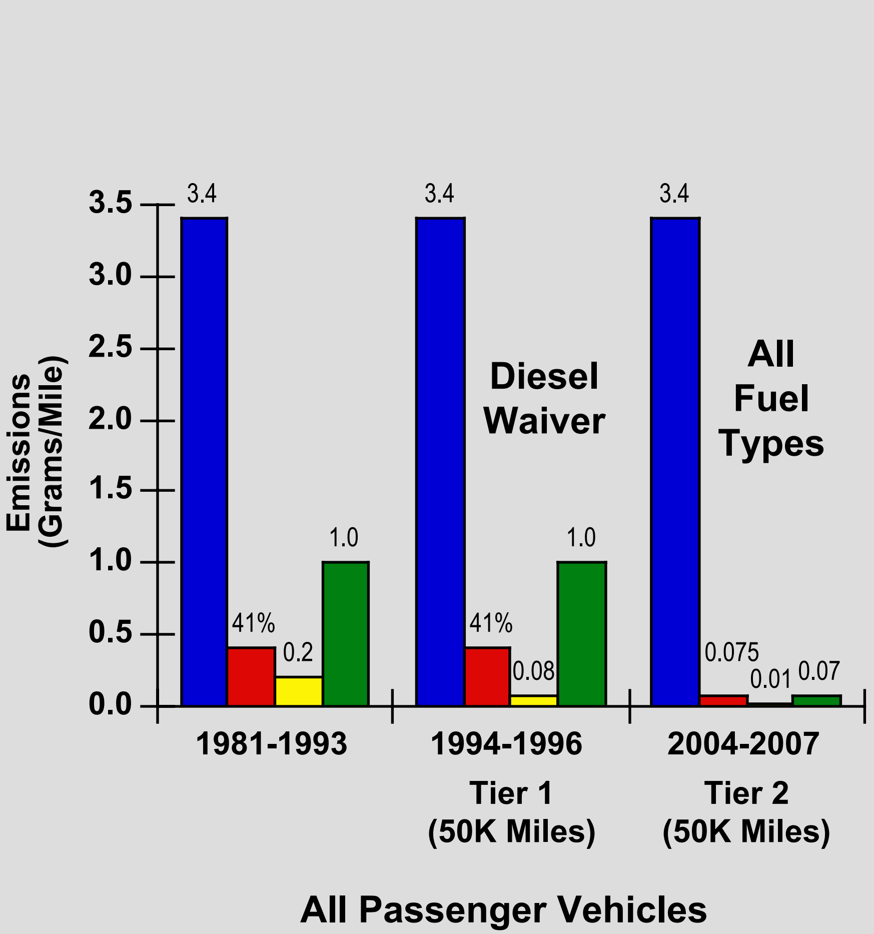
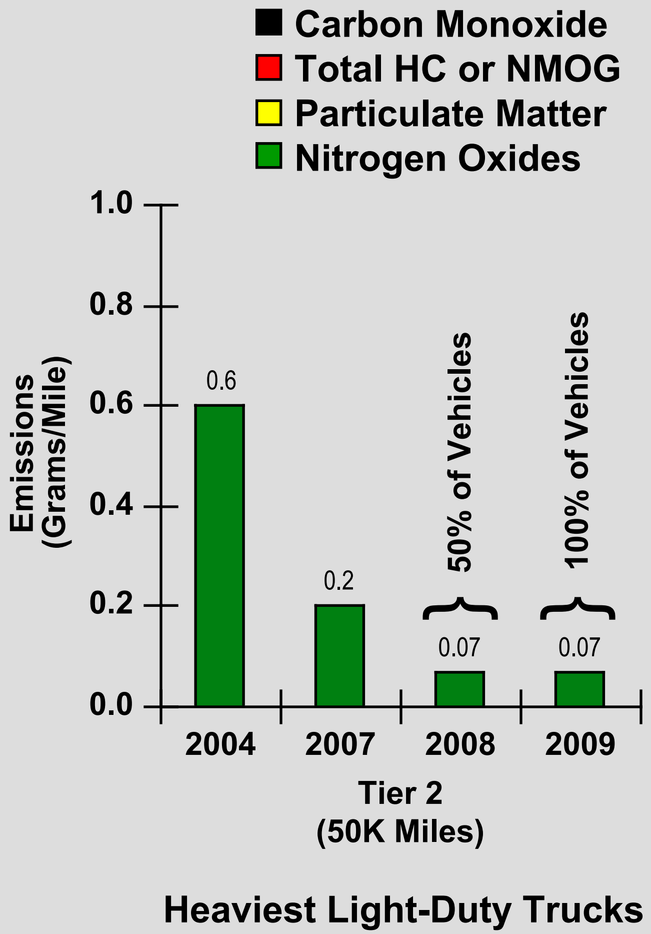
Rod Borup, Michael Inbody, Byron Morton and Lee Perry

Los Alamos National Laboratory

ESA-AET

Clean Air Act Is Driving Technology for Automotive Exhaust Applications





Lean NOx Catalysis

- Increasing energy efficiency in the transportation sector has greatest potential for reducing CO_2 emissions by 2010
- Lean burn engines are candidates for future vehicles
  - 3 - 4x fuel economy
  - Equates to 20% reduction in US CO_2 emissions
- Requires reduction of NO_x under oxidizing (12% O_2) conditions
- Conventional Three-Way catalysts are ineffective for NO_x reduction in presence of O_2

NOx Reduction Chemistry

- Direct decomposition
  - 2NO ----> $N_2 + O_2$
- SCR (Selective Catalytic Reduction):
  - $3NO + 2NH_3$ ----> $5/2\ N_2 + 3H_2O$
  - $4NO + 4\ NH_3 + O_2$ ----> $4N_2 + 6H_2O$
  - NO reduction competes with NH_3 oxidation to NO in presence of O_2
- NOx Reduction in oxygen atmosphere
  - $NO + HC + O_2$ ----> $N_2 + CO_2 + H_2O$
  - Challenge lies in reducing NOx in oxidizing atmosphere

- Avoid putting NH_3, HCN, NO_2, SO_3, N_2O, RNO_2, RCHO, RCOOH, RCN, …. out the tailpipe

Formation of Reductants for NOx reduction

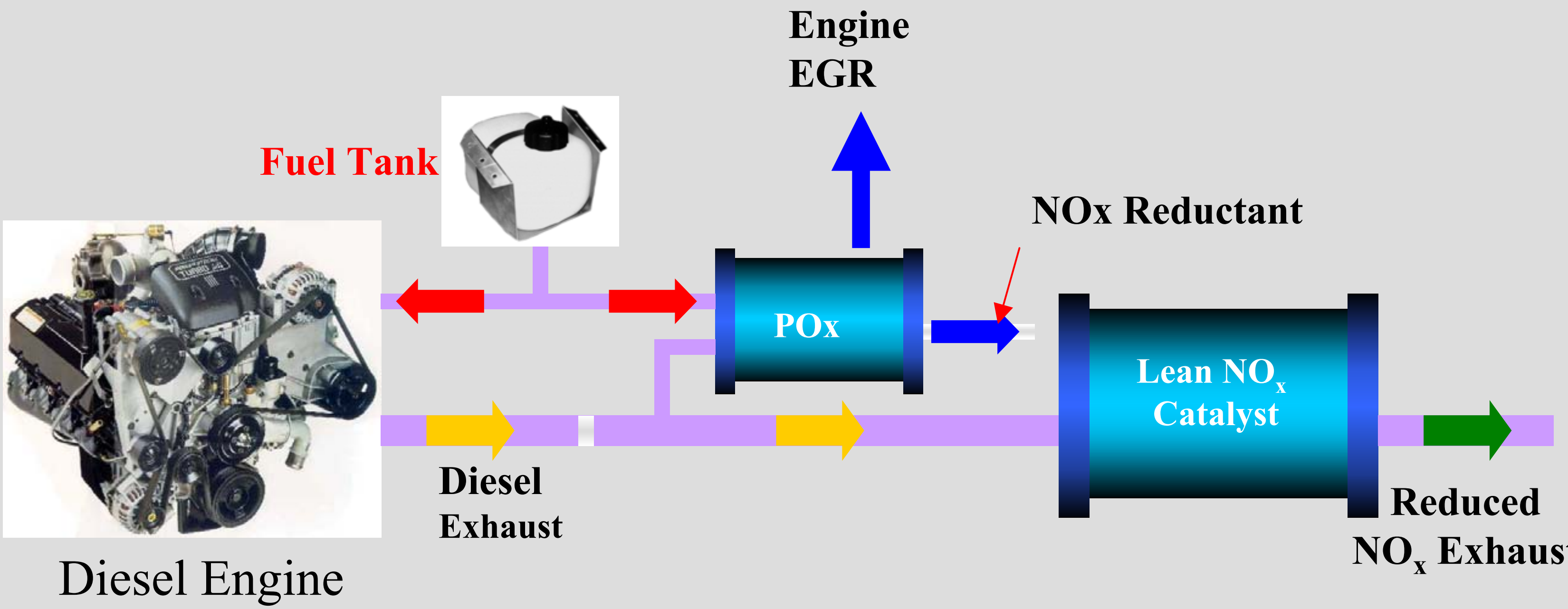
- Form NOx reductants by partial oxidation of diesel fuel
- POx - Rich fuel burn:
  - (O/C = 1)
    - $C_nH_{(2n+2)} + {}_{(n/2)}O_2 \text{-->} nCO + {}_{(n+1)}H_2$
  - (O/C < 1)
    - $C_nH_{(2n+2)} + {}_{(m/2)}O_2 \text{-->} mCO + C_{(n-m)}H_{2(n-m)} + H_2$
  - POx effluent includes:
    - H_2, CO, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8

- Propene known to catalyze NOx reduction reaction
  - reductant for plasma, zeolites (somewhat similar to NH_3 SCR)
- H2 / CO known to reduce NOx adsorbents

NOx Reduction Project Objectives

- Show proof of concept for reformer - hydrocarbon reduction of NOx
- Develop methods for the on-board generation of reductants
  - Reforming of diesel fuel to form:
    - Reductants for lean NOx catalysis
    - Regeneration of NOx adsorbers
  - Optimize the reductant composition
    - Hydrogen … Propene …
    - Examine and understand reductant interactions with NOx catalysis
  - Develop diesel reforming technology suitable for on-board reforming
    - Durability
    - Start-up
    - Vehicle integration (air and water feed/sources)
    - Cost

Diesel Reformer Vehicle System Integration



Integration Issues:

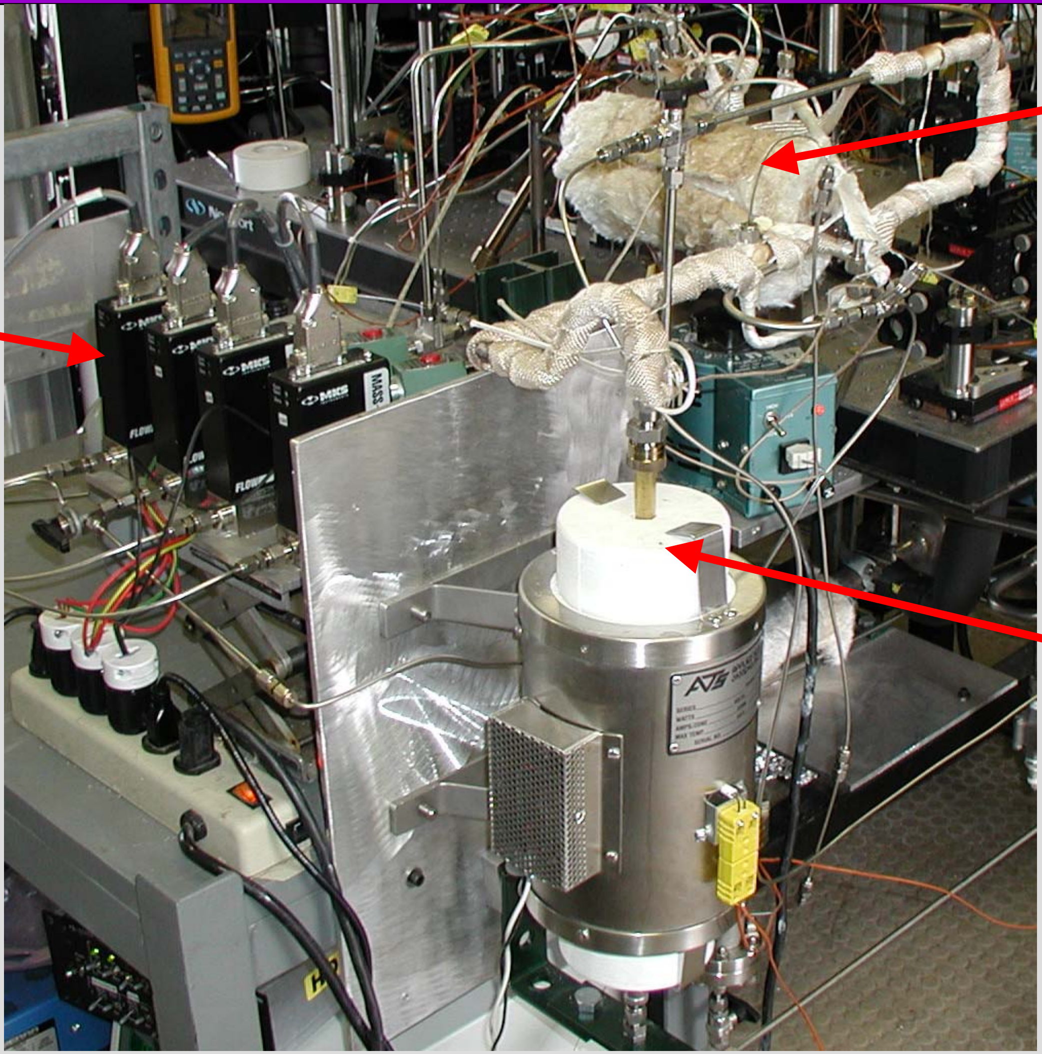
Oxidant (Air or Engine Exhaust [12 – 17 % O_2])

On-board water (low water operation, zero water start-up)

SOFC Anode recycle/Engine exhaust add water

Diesel Reductant – NOx Reduction Catalyst Setup

MFC's
For simulated
Diesel exhaust
mixing

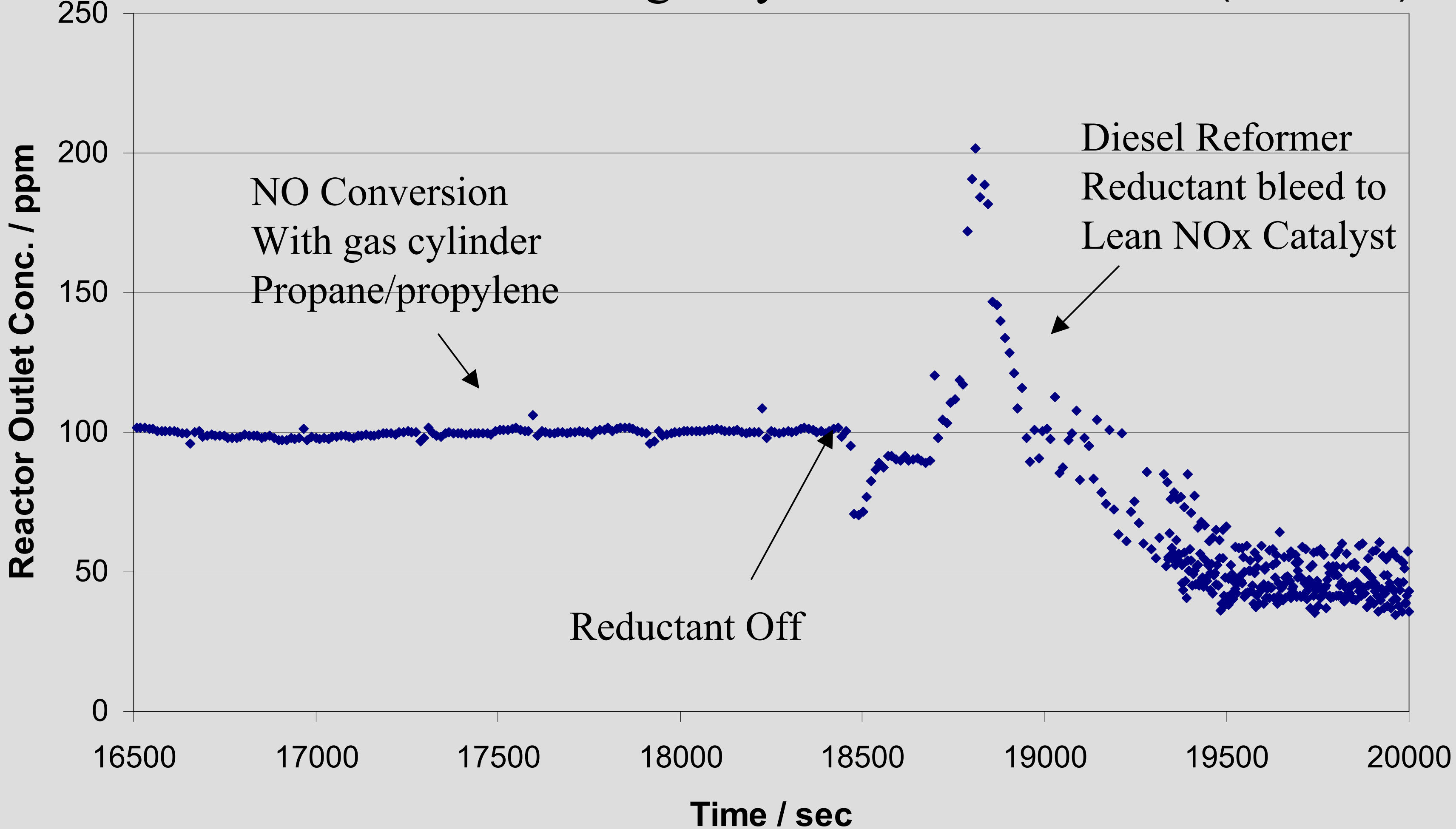


Diesel
Reformer

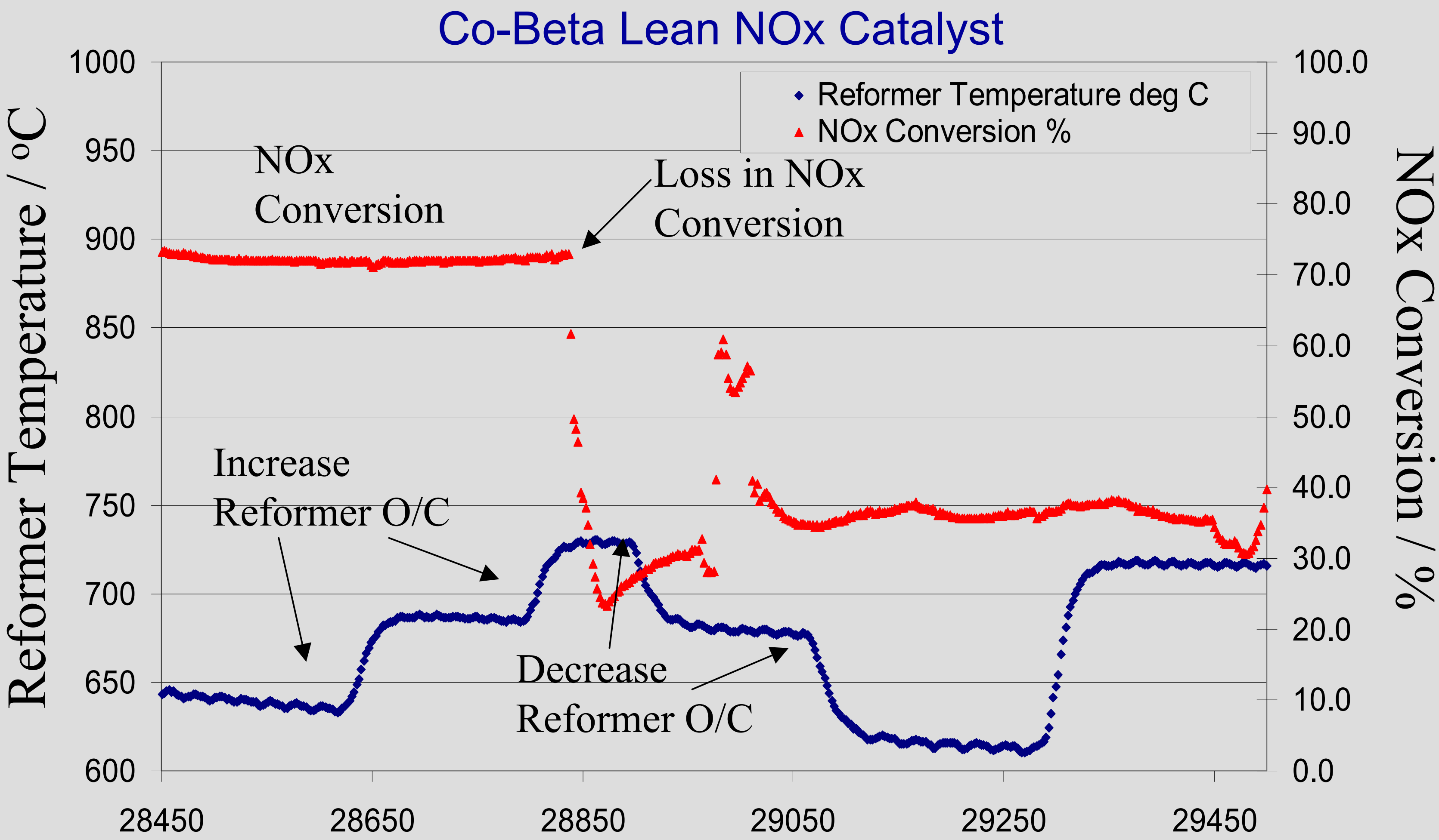
Lean NOx
Catalyst

NOx Reduction

with reductant from gas cylinder and reformer (Co-Beta)

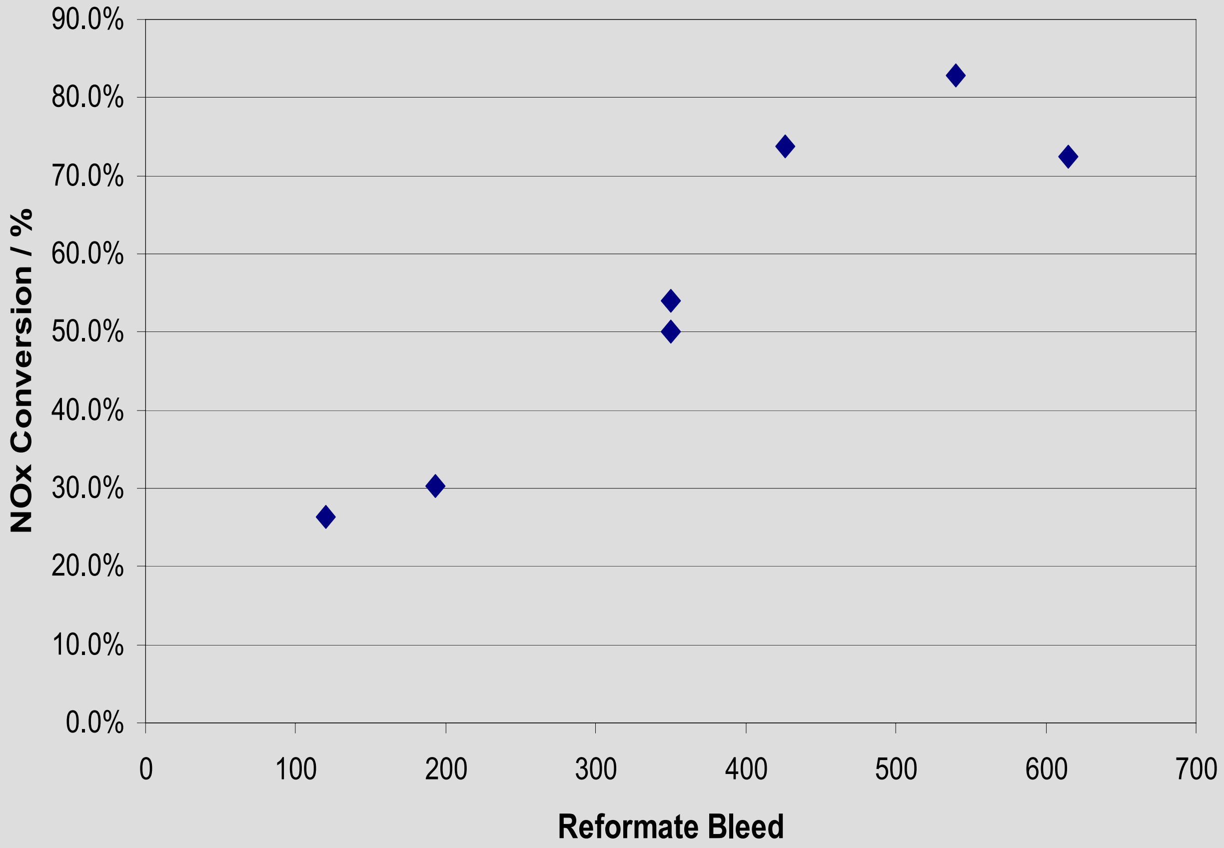


Reformer Operating Condition Effect on NOx Reduction



NOx Conversion with Hydrocarbon Bleed from Diesel Reformer

(Co-Beta Lean NOx Catalyst)



Conditions:

Diesel Reformer:

Fuel: Kerosene

15.8 % O2 as oxidant

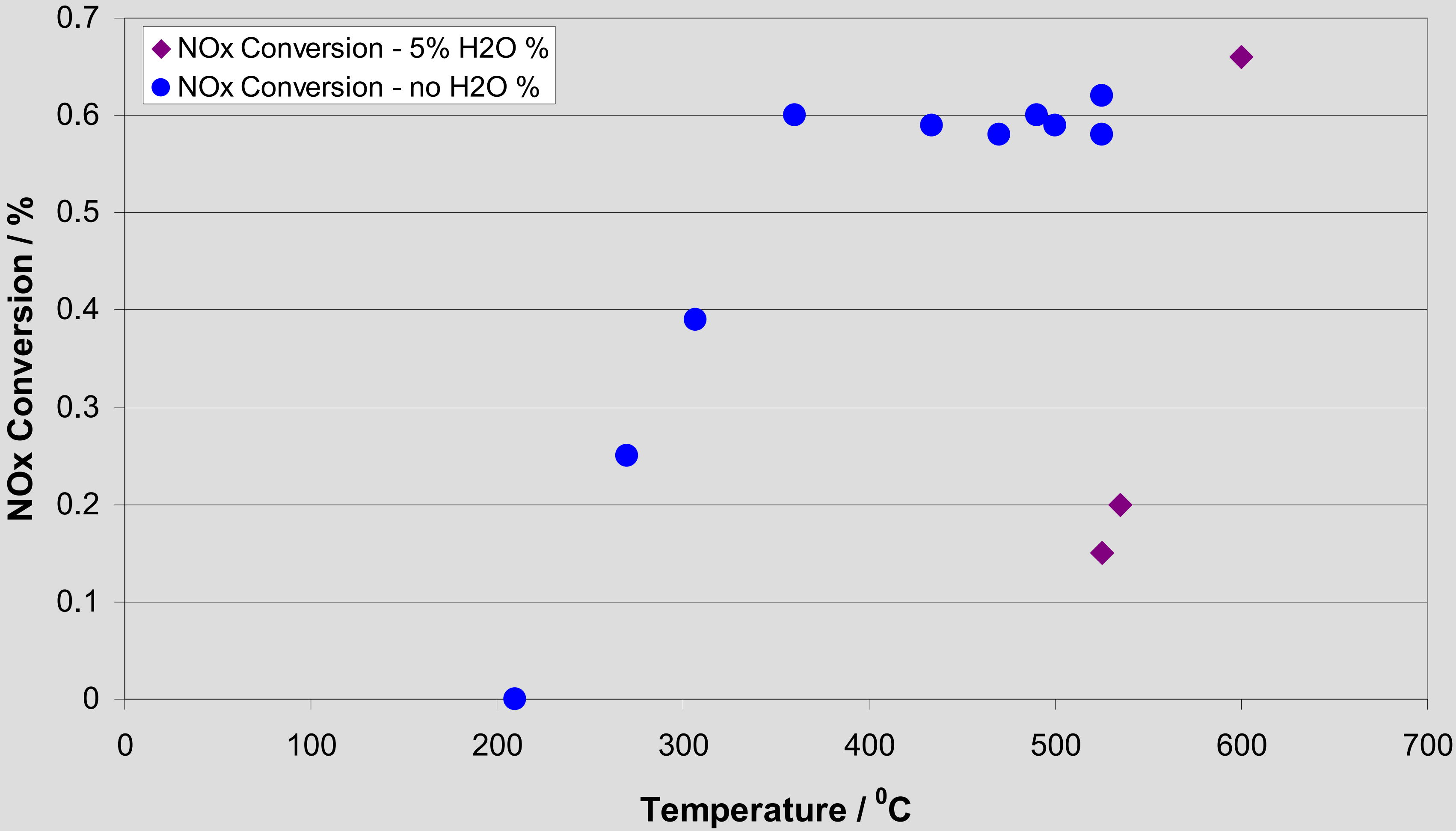
O/C = 0.85

S/C = 0.0

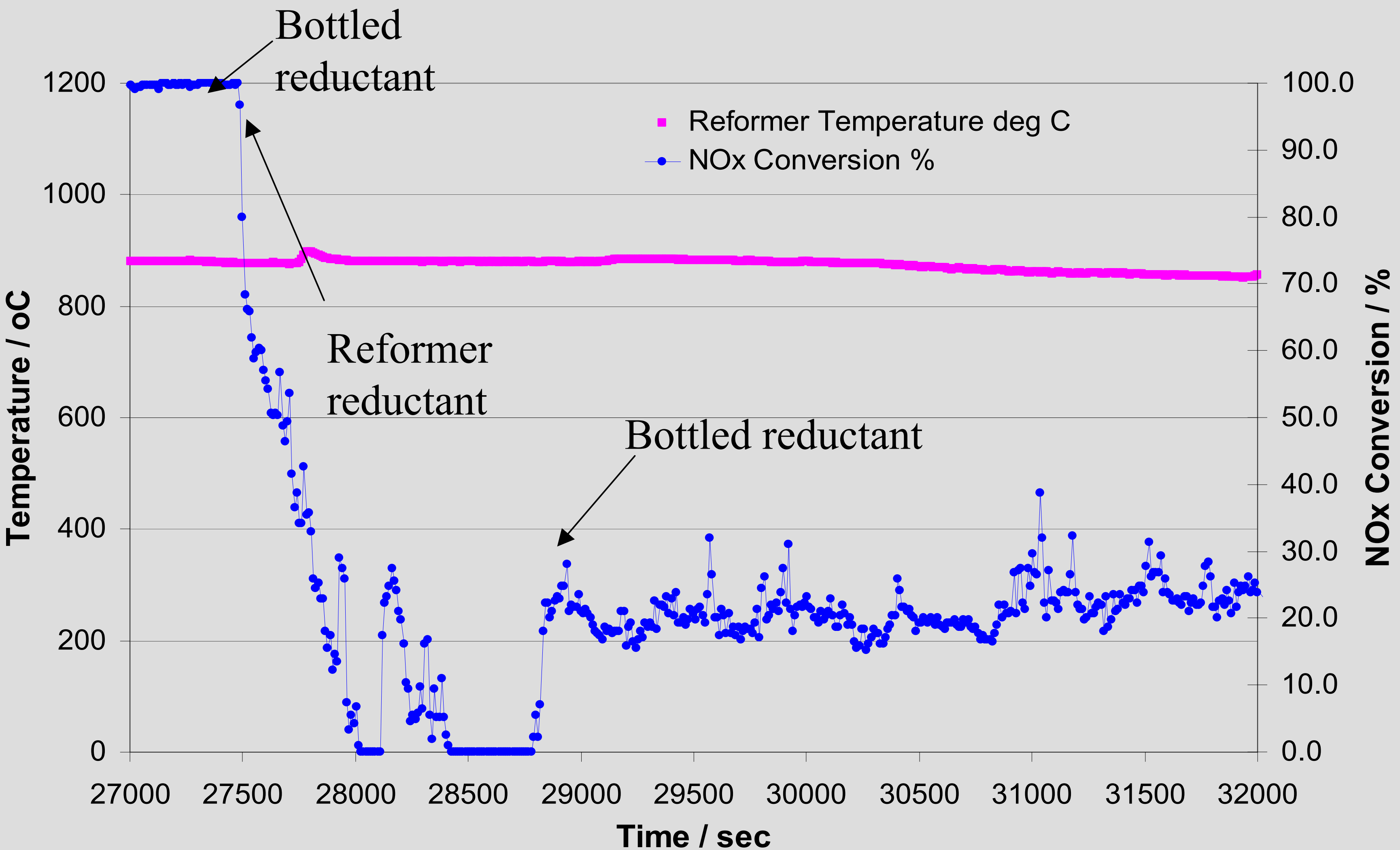
NOx Reactor

263 ppm NOx in 566 sccm flow

NOx Conversion with Hydrocarbon Bleed from Diesel Reformer (Co-Beta)



NOx Reduction with Co-FER Lean NOx Catalyst



Calculated Theoretical Fuel Penalty (based on reformer outlet concentrations)

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Lean NOx catalysts: regenerate with unsaturated hydrocarbons

Assumptions:

$9NO + C_3H_6 \rightarrow 9/2N_2 + 3CO_2 + 3H_2O$

250 ppm NO engine out exhaust
1 lb/min exhaust
15.6 moles/min exhaust
0.004 moles/min NO
$C_{13.5}H_{22}$ Fuel

$C_{13.5}H_{22} + O_2 \rightarrow 13.5CO + 11H_2 + (0.05\ \%\ C_3H_6)$
Reductant Stoich = 2.0

Based on C3H6 + C2H4
1.6% fuel penalty

NOx adsorbers: regenerate with H2 + CO

Assumptions:

$2NO + 2H_2 \rightarrow N_2 + 2H_2O$
$2NO + CO \rightarrow N_2 + 2CO_2$

250 ppm NO engine out exhaust
1 lb/min exhaust
15.6 moles/min exhaust
0.004 moles/min NO

$C_{13.5}H_{22}$ Fuel
Reformer O/C = 1.0

$C_{13.5}H_{22} + O_2 \rightarrow 13.5CO + 11H_2$
Reductant Stoich = 2.0

1.0 % fuel penalty

Experimental Fuel Penalty NOx Reduction with Reformer Bleed

For NOx reduction of 50 – 80%

Experimental Fuel Penalty over Co-Beta Catalyst

For various vehicle assumptions: fuel penalty is ~ 3 % - 6 %

Total Vehicle Exhauste Flowrate	15.68378	slpm
Based on:		
Simulated Exhaust Flowrate	0.566	slpm
% flow reductant	0.209497	
Reductant flowrate required	3.285708	slpm
Fuel Requirement (de-NOx)	0.633405	g/min fuel
Fuel Requirement (vehicle)	11.36364	g/min fuel
Fuel penalty	**5.57%**	
Based on:		
Simulated Exhaust Flowrate	0.849	slpm
% flow reductant	0.209497	
Reductant flowrate required	1.997329	slpm
Fuel Requirement (de-NOx)	0.385037	g/min fuel
Fuel Requirement (vehicle)	11.36364	g/min fuel
Fuel penalty	**3.39%**	

Conclusions
Reductant Reduction of NOx

- **Cobalt-beta-zeolite and Cobalt-Ferrite lean-NOx catalysts**
  - **drastically different results with reductant from reformer**

- **NOx reduction with Standard Lean NOx conditions**
  T = 500 C (263 ppm into lean NOx catalyst)
  - **With no hydrocarbon injection - No NOx reduction**
  - **With propylene injection (from cylinder) - 60 % NOx reduction**

- **NOx reduction with reductant bleed from reformer**
  - **Demonstrated NOx reduction with reformer injection**
  - **NOx conversion varies with injection rate**
    - **20% to 80 % NOx conversion**

- **With POx air cycling**
  - **O/C = 1.0 to O/C = 0.0 (reformer temperature > 700 ^{0}C)**
  - **Demonstrate NOx reduction > 70%, with up to 96% conversion**

→Very high fuel penalty

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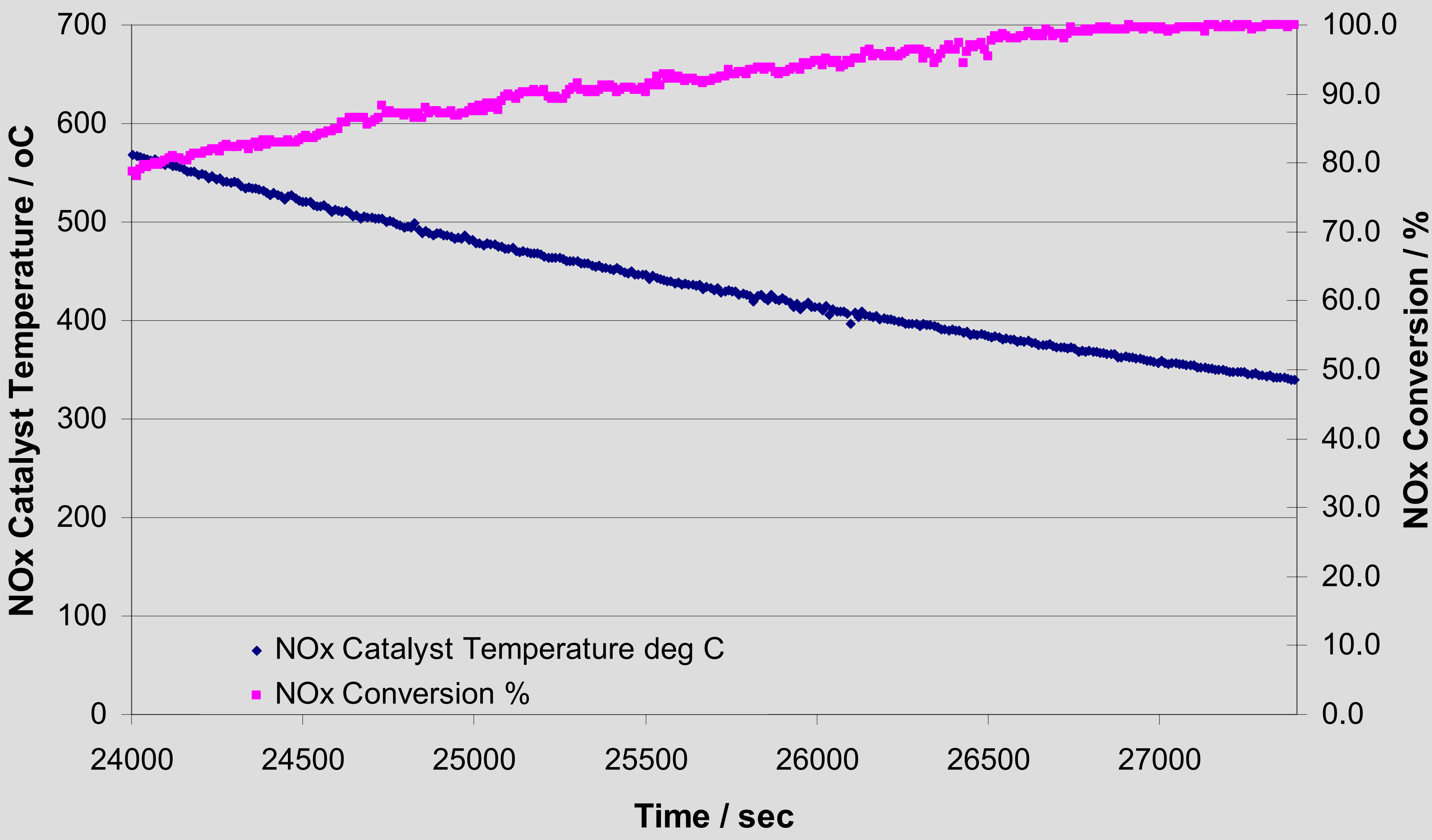
NOx Reduction with 'Bottled Reductant' (Co-FER)

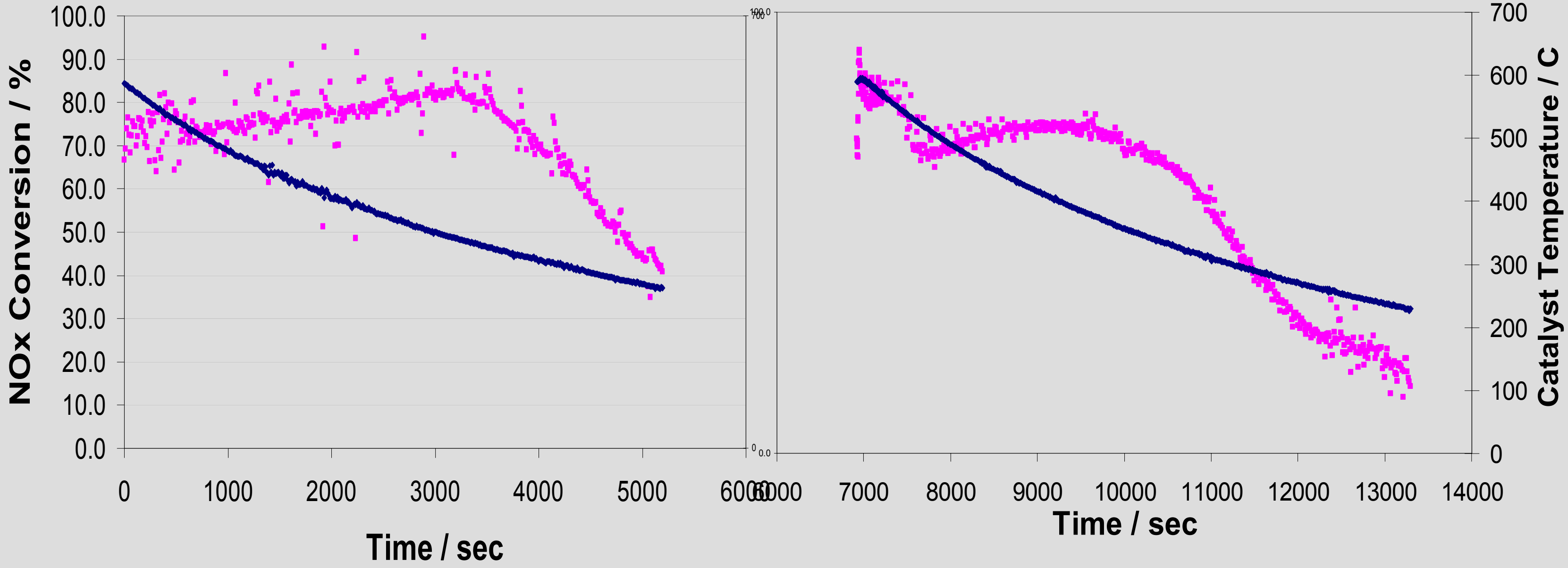


Water/Temperature Effect on NOx Reduction

Co-Beta Zeolite catalyst

1.4 % H2O

5.8 % H2O



NOx reductant by gas cylinder C3H6/C3H8

LANL Diesel Reforming - deNOx

- Constructed NOx reduction sized POx reactors
  - Initial testing with Dodecane, Kerosene
  - Ethylene and Propylene production of 2.0 % and 1.0 %
    - Operate with 'simulated' engine exhaust for oxidant
    - Incorporate diesel POx with :
      - Lean NOx catalysts
      - NOx adsorbers (FY2002?)

- **Reactor Conditions:**

  Fuel: Dodecane
  Residence Time: 43 msec
  O/C = 1.2
  S/C = 1.9
  T_{out} = 830 ^{o}C

C2H4 (ethylene): 1.0 %
C3H6 (propylene): 0.05 %

- **Reactor Conditions:**

  Fuel: Kerosene
  Residence Time: 43 msec
  O/C = 1.0
  S/C = 0.0
  T_{out} = 1100 ^{o}C

C2H4 (ethylene): 1.8 %
C3H6 (propylene): 1.5 %